A Simple Oleanlic Acid Derivative as Potent Organogelator

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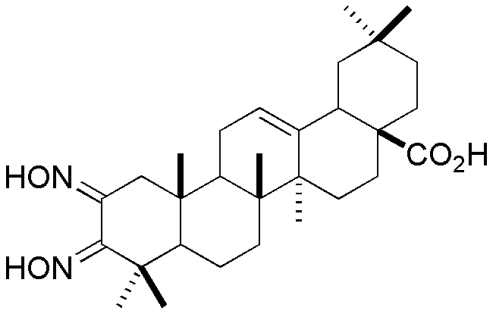
Synthesis and Structure Data of 2,3-dihydroxyimino-oleanic acid (6)



6

Synthesis of 2, 3-dihydroxyimino-oleanic acid (6): The synthesis of **6** was carried out by the reported method.[1] The purity of **6** was verified by NMR spectroscopy, thin-layer chromatography, mass spectroscopy and melting point (m.p. 209-213°C, ref.[1] 208-212°C). All the experimental data of the isolated products were coincident with those previously reported. [1]

ESI-MS(+) : m/z=499 $[M+H]^+$, 1019 $[2M+Na]^+$.

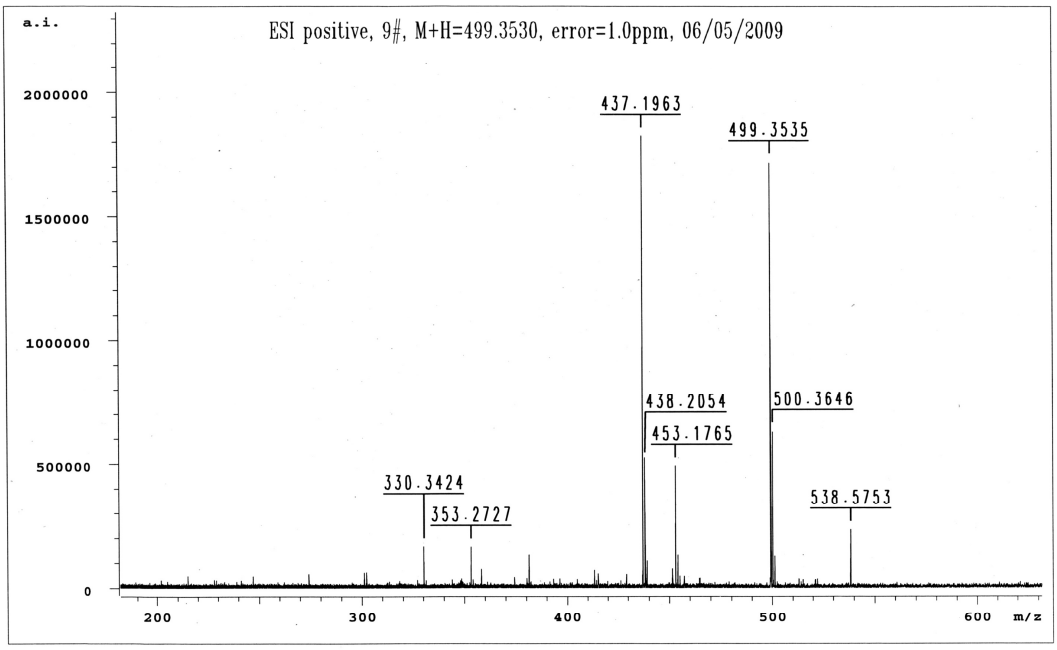
ESI-MS(-) : m/z=497 $[M-H]^-$, 995 $[2M-H]^-$, 1493$[3M-H]^-$.

HRMS(ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{46}N_2O_4$: 499.3458; found: 499.3535.

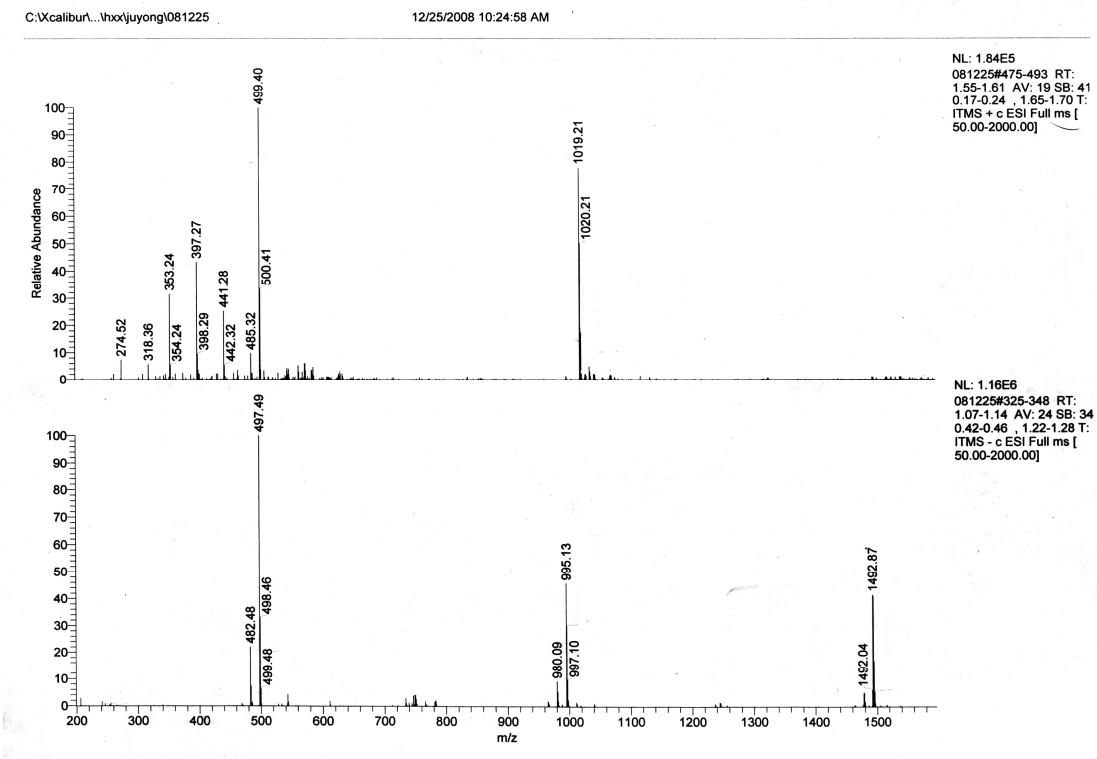
^{1}H NMR (300MHz, pyridine-d_5): 5.53 (m, 1H, 12-CH), 3.39(d, 1H, 1-CH_2, J=17.19Hz), 3.34(m, 1H, 18-CH),1.10, 1.03, 1.03, 1.29, 1.38, 1.40, 1.40 (7×S, 7×3H , 23, 24, 25, 26, 27, 29, 30-CH_3).

^{13}C NMR (75MHz, pyridine-d_5): 180.00(28-C), 154.63(3-C), 152.36(2-C), 144.49(13-C), 122.12 (12-C).

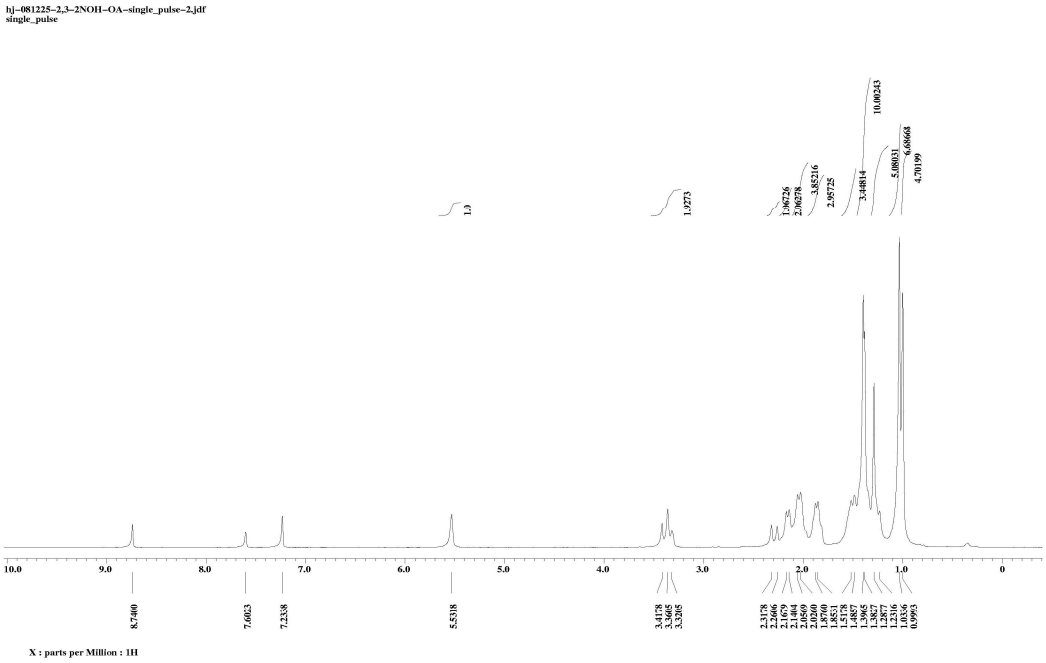
1. HRMS (ESI) Spectra of 2,3-dihydroxyimino-oleanic acid (**6**)



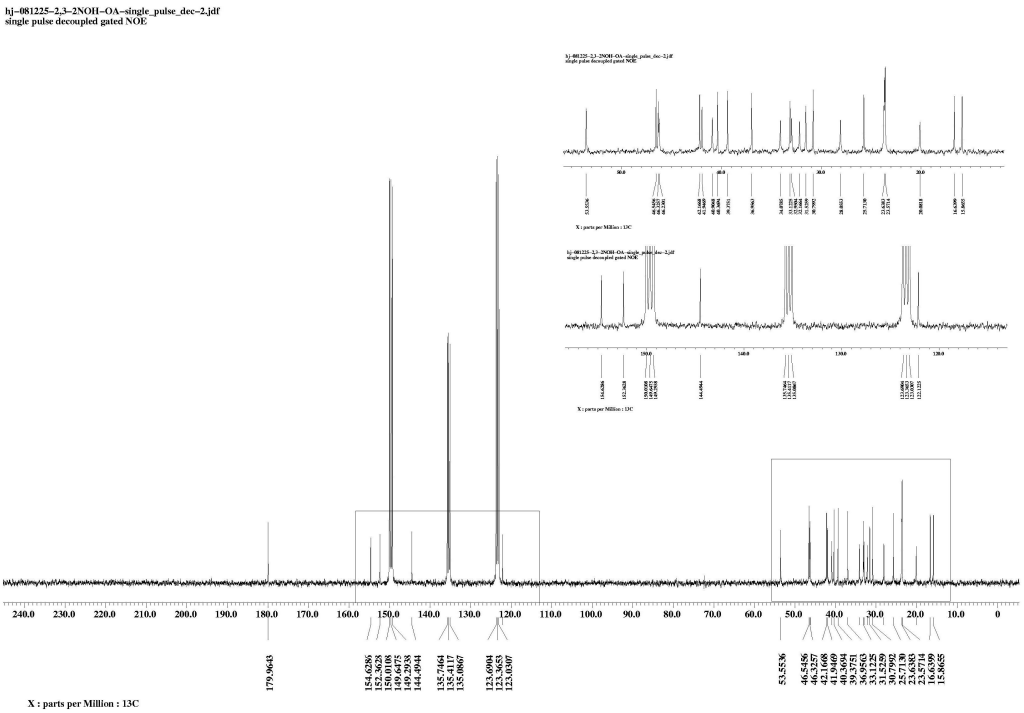
2. ESI-MS Spectra of 2,3-dihydroxyimino-oleanic acid (**6**)



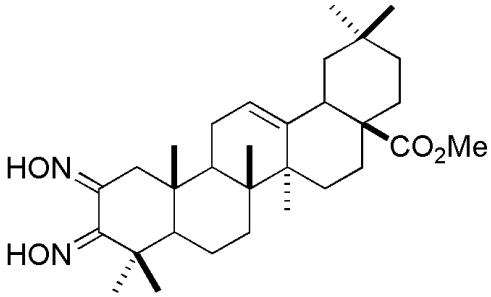
3. ^{1}H NMR Spectra (pyridine-d_5) of 2,3-dihydroxyimino-oleanic acid (**6**) (300MHz)



4. ^{13}C NMR Spectra (pyridine-d_5) of 2,3-dihydroxyimino-oleanic acid (**6**) (75MHz)



Synthesis and Structure Data of 2,3-dihydroxyimino-28-methyl oleanolate (7)



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Synthesis of 2, 3-dihydroxyimino-28-methyl oleanolate (7): The synthesis of **7** was carried out by the reported method.[2] The purity of **7** was verified by NMR spectroscopy, thin-layer chromatography, mass spectroscopy and melting point (m.p. 185-187°C, ref.[2] 185-188°C). All the experimental data of the isolated products were coincident with those previously reported. [2]

ESI-MS(+) : m/z=513 $[M+H]^+$, 535 $[M+Na]^+$, 1047 $[2M+Na]^+$, 1560 $[3M+Na]^+$.

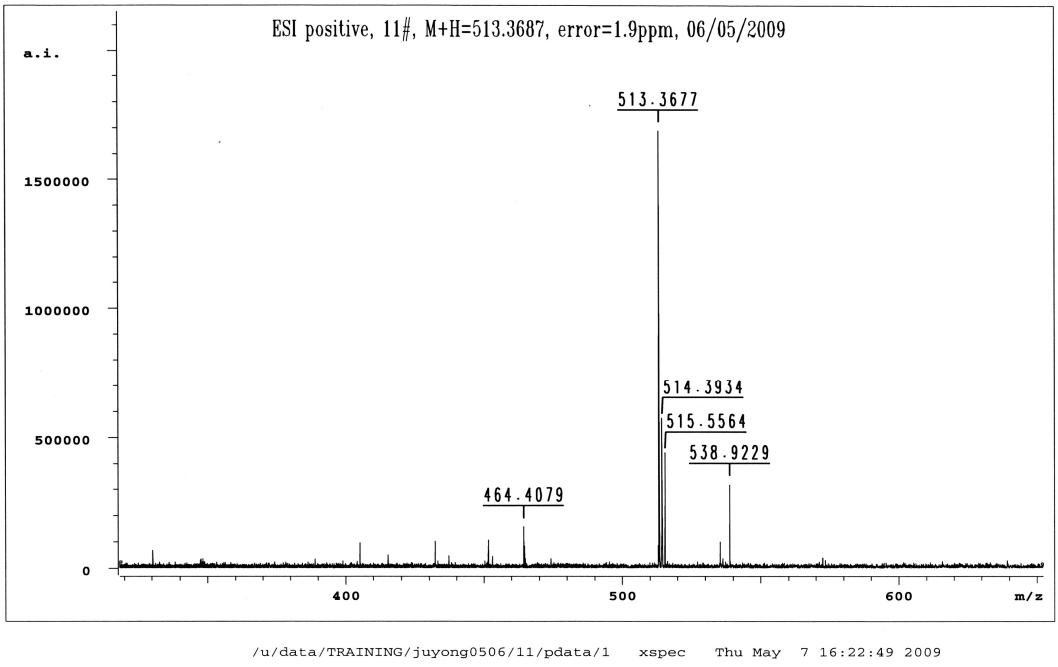
ESI-MS(-) : m/z=511 $[M-H]^-$, 1023 $[2M-H]^-$.

HRMS(ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{48}N_2O_4$: 513.3614; found: 513.3677.

^{1}H NMR (300MHz, $CDCl_3$): 5.31(m, 1H, 12-H), 3.61(s, 3H, 31-CO_2CH_3), 3.13(d, 1H, 1-CH_2, J=17.85Hz), 2.86(m, 1H, 18-CH), 0.75, 0.88, 0.90, 0.91, 1.12, 1.20, 1.24(7×S, 7×3H , 23, 24, 25, 26, 27, 29, 30-CH_3).

^{13}C NMR (75MHz, $CDCl_3$): 178.74(28-C), 153.79(3-C), 153.34(2-C), 143.68(13-C), 122.23(12-C).

1. HRMS (ESI) Spectra of 2,3-dihydroxyimino-28-methyl oleanolate (**7**)



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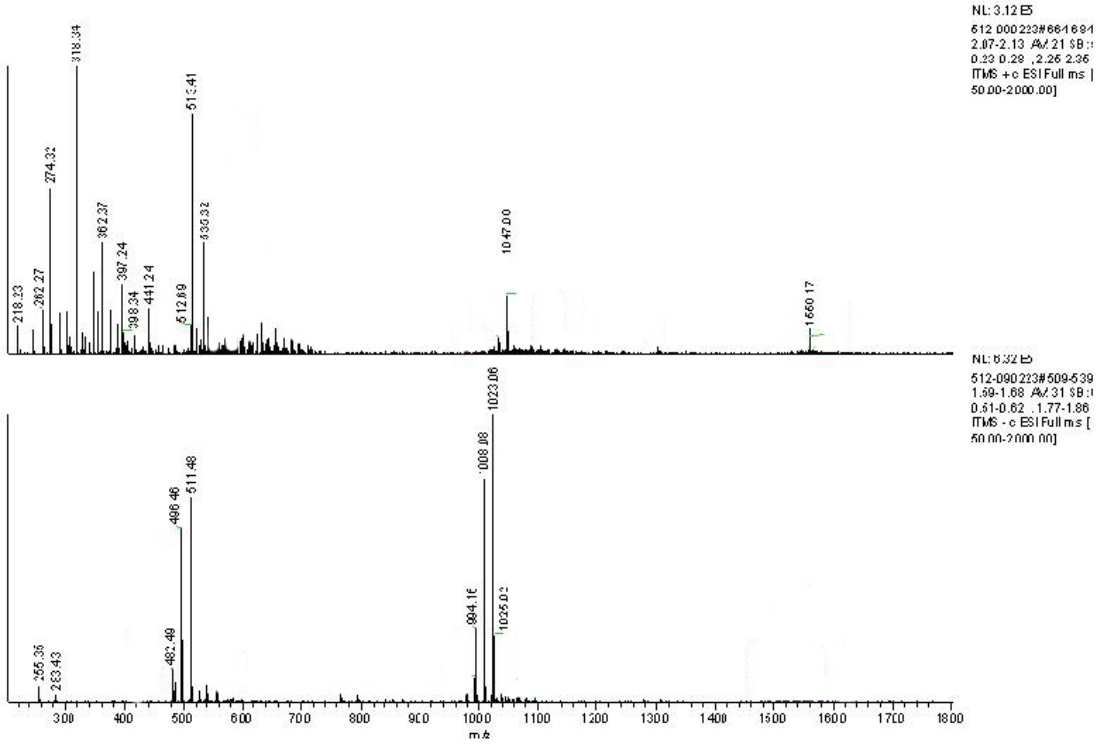
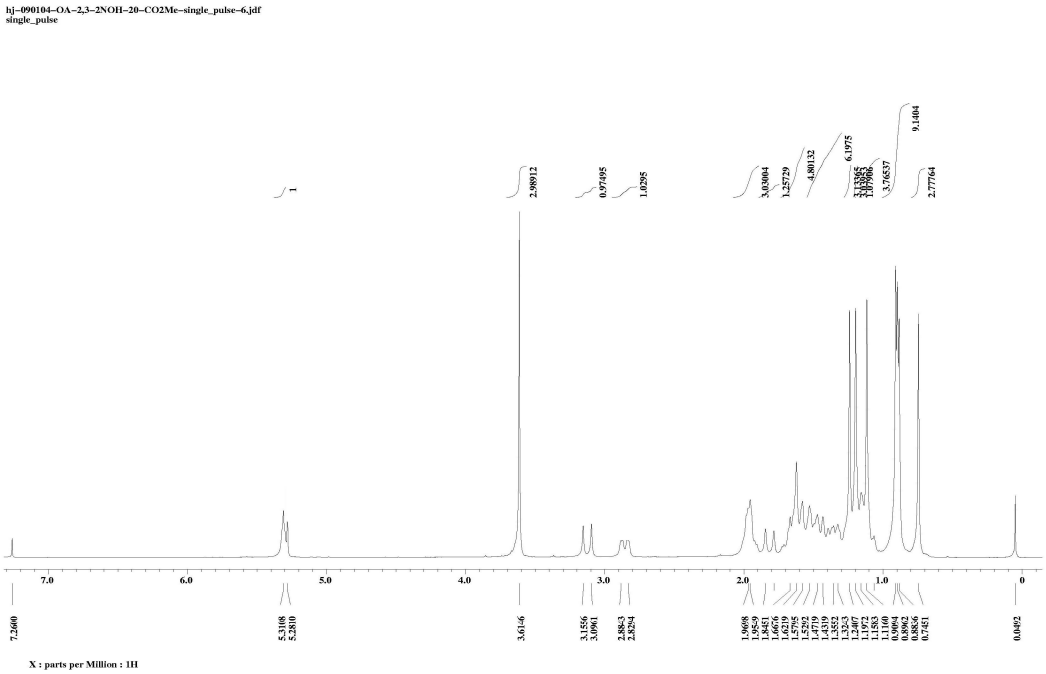
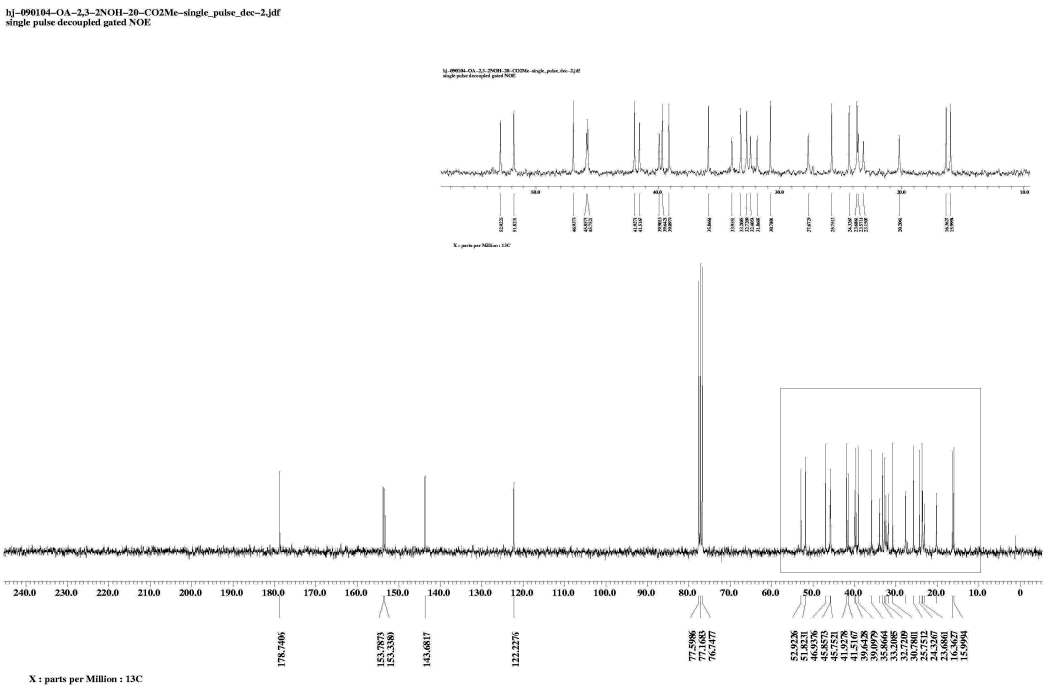


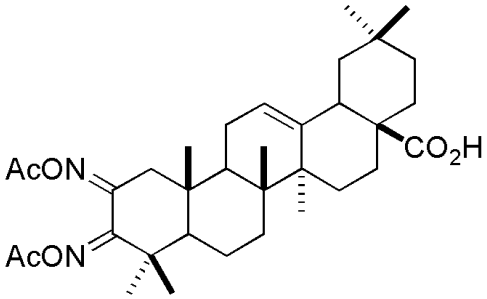
3. ^{1}H NMR Spectra ($CDCl_3$) of 2,3-dihydroxyimino-28-methyl oleanolate (**7**)(300MHz)



4. ^{13}C NMR Spectra ($CDCl_3$) of 2,3-dihydroxyimino-28-methyl oleanolate (**7**) (75MHz)



Synthesis and Structure Data of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (8)



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Synthesis of 2, 3-dione O, O-diacetyl-dioxime-oleanic acid (8): 300mg (0.60 mmol) **6** and 15mg (0.12mmol) DMAP were dissolved in 10ml pyridine, then 1.33ml (12.05mmol) acetic anhydride was added slowly. After the mixture stirred for 24h at r.t, the solvent was evaporated. The residue was dissolved in dichloromethane and washed with water, saturated brine, then dried over $MgSO_4$ and evaporated. Purification by flash chromatography (DCM: Methanol =70:1) afforded **8** as white solid (184mg, 51%).

m.p: 149-151°C.

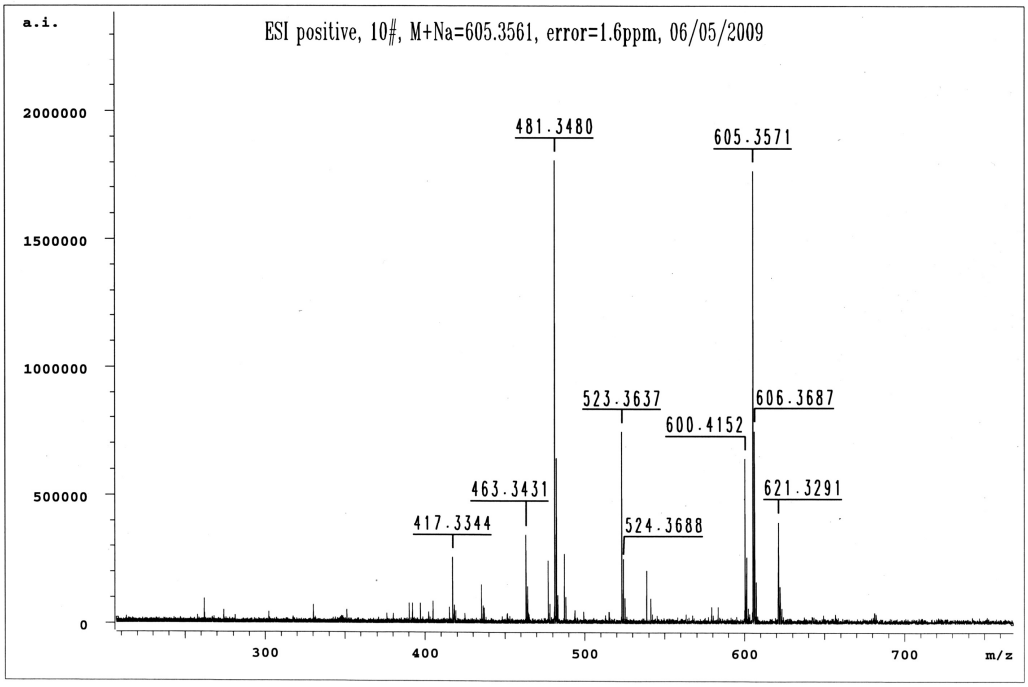
ESI-MS (+) : m/z=605 $[M+Na]^+$, 1087 $[2M+Na]^+$, 1770 $[3M+Na]^+$.

ESI-MS (-): m/z=581 $[M-H]^-$, 1063$[2M-H]^-$, 1744 $[3M-H]^-$.

HRMS(ESI): m/z $[M+Na]^+$ calcd for $C_{34}H_{50}N_2O_6$: 605.3567; found: 605.3571.

^{1}H NMR ($CDCl_3$, 300 MHz): 5.28(m, 1H, 12-H), 2.81(d, 1H, 1-CH_2, J=16.47Hz), 2.21, 2.10(2S, 2×3H, $NOCOCH_3$), 0.75, 0.88, 0.90, 0.96, 1.12, 1.22, 1.24(7S, 7×3H , 23, 24, 25, 26, 27, 29, 30-CH_3); ^{13}C NMR($CDCl_3$, 75MHz): 184.04 (28-C), 168.71, 168.64 (2C, NO<u>C</u>OCH_3), 165.06 (3-C), 157.67 (2-C), 144.01 (13-C), 121.70 (12-C).

1. HRMS (ESI) Spectra of 2,3-dione O, O-diacetyl-dioxime-oleanic acid (**8**)



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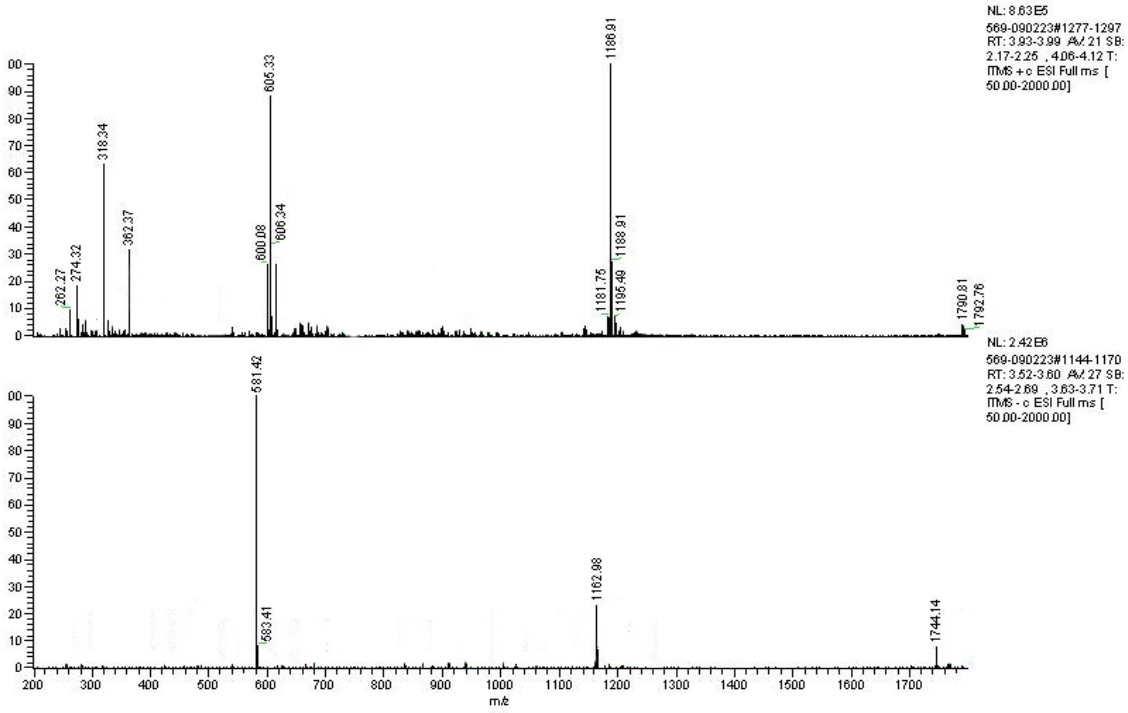

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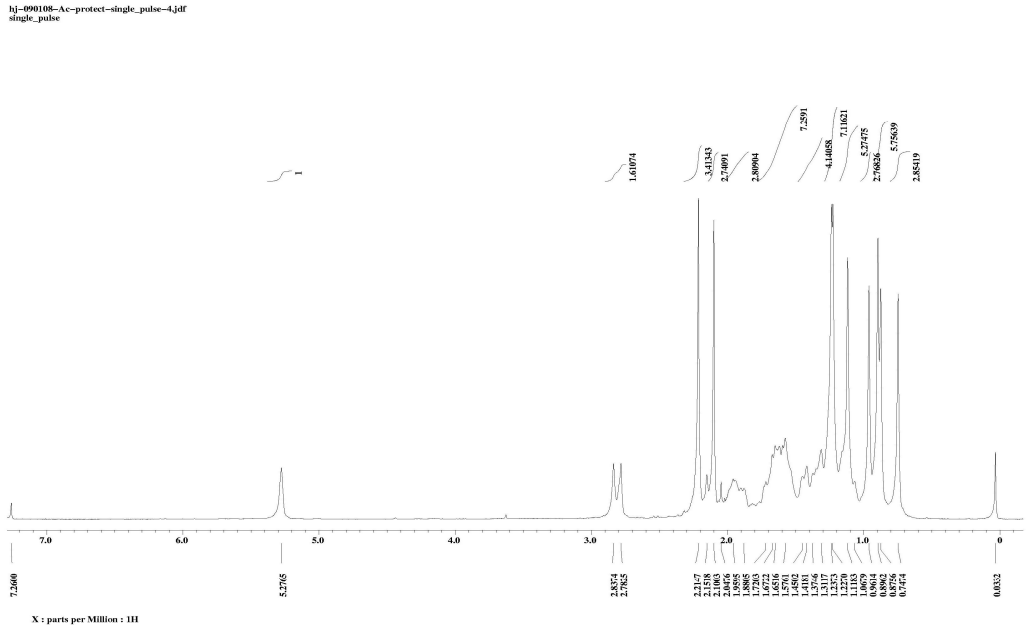

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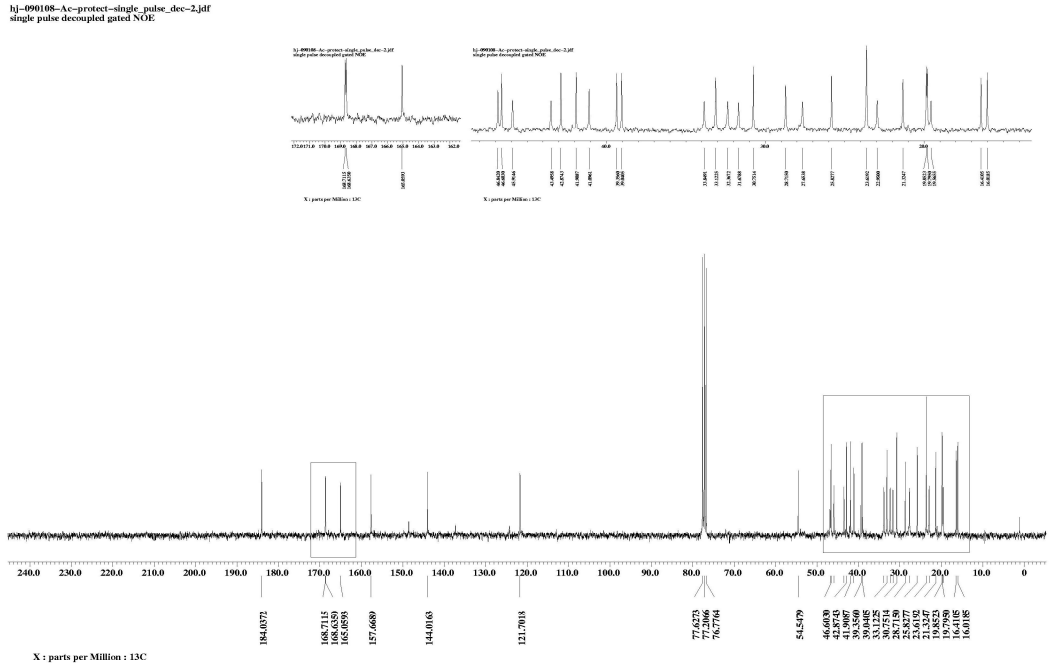


Thermodynamic Parameters of Gel 2,3-dihydroxyimino-oleanic acid (6) [3, 4]

The thermoreversible melting of a two-component gel can be expressed as:

Gel $\rightleftharpoons$ liquid

For one-component gel, the equilibrium constant can be expressed as:

K = [Gelator] / [Gel]

Assuming unit activity of the gel and taking concentration of the solution to be equal to the dissolved concentration of the gelator, the equilibrium constant can be expressed as:

K = [Gelator].

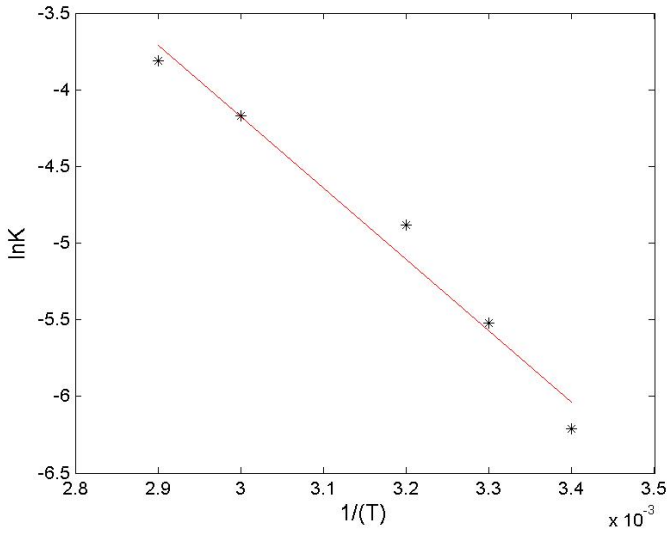
The Gibbs free energy changed during gel melting can be expressed as:

$\Delta G^o = - \Delta RTlnK = \Delta H^o - T\Delta S^o$,

Hence, $lnK = - \Delta H^o /R (1/T) + T\Delta S^o /R$

The gel melting temperature (T_{gel}) increases with the concentration of the "solutes". A plot of lnK *vs* 1/T allowed us to calculate the thermodynamic parameters.

Benzene



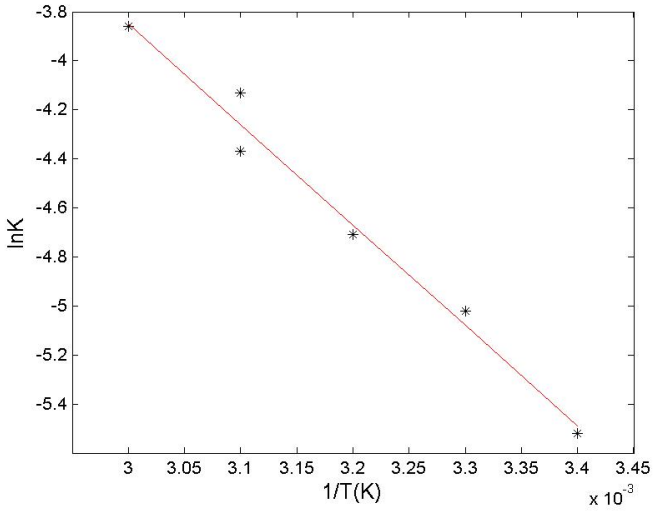
$$\ln K = -4.6547\times10^3 \frac{1}{T} + 9.7907, \quad r = 0.97546$$

□$\Delta H^o/R$ = -4654.7, ΔH^o =38.7kJ/mol;

□$\Delta S^o/R$=9.7907, ΔS^o=81.4 J/mol/K

□$\Delta G^o = \Delta H^o - T\Delta S^o$=38.7-297×0.0814 = 14.5kJ/mol

Toluene



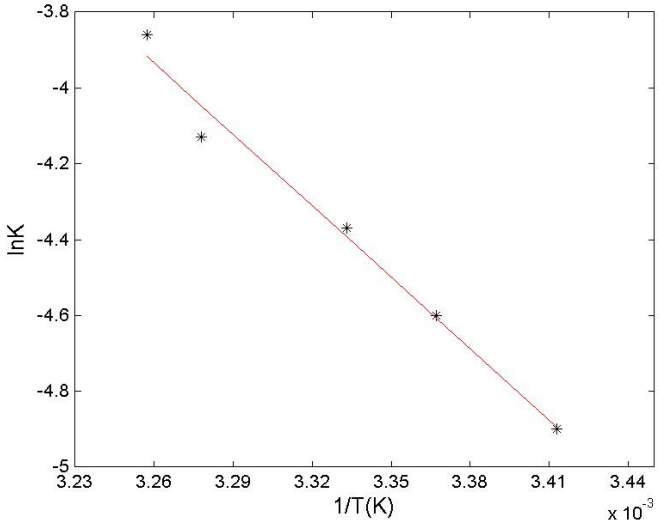
$$\ln K = -4.1000\times10^{3}\frac{1}{T} + 8.4500\,,\ \mathrm{r}=0.98104$$

□$\Delta H^{o}/R$ = -4100.00, ΔH^{o}=34.1kJ/mol;

□$\Delta S^{o}/R$=8.45, ΔS^{o}=70.3 J/mol/K

□ΔG^{o}=ΔH^{o} - $T\Delta S^{o}$=34.1-297×0.0703 = 13.2kJ/mol

Chloroform



$$\ln K = -6.2816\times10^{3}\frac{1}{T} + 16.544\,,\ \mathrm{r}=0.98357$$

□$\Delta H^o/R$=-6281.6, ΔH^o =52.2 kJ/mol;

□$\Delta S^o/R$=16.544, ΔS^o=137.5 J/mol/K

□$\Delta G^o = \Delta H^o - T\Delta S^o$=52.2-297×0.1375=11.4kJ/mol

Table 1. Thermodynamic parameters (ΔH°, ΔS° and ΔG°) of gel **6** in various solvents at 298K

Solvent	ΔH^o kJ/mol	ΔS^o J/mol/K	ΔG^o kJ/mol
Benzene	38.7	81.4	14.5
Toluene	34.1	70.3	13.2
Chloroform	52.2	137.5	11.4

References

1 M. S. Y. Khan, S. Ahmad, M. R. Yadav and D. P. Jindal, *Journal of the Indian Chemical Society*, 1990, **67**, 330-331.

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3 D. Rizkov, J. Gun, O. Lev, R. Sicsic and A. Melman, *Langmuir*, 2005, **21**, 12130-12138.

4 B. G. Bag, G. C. Maity and S. K. Dinda, *Organic Letters*, 2006, **8**, 5457-5460.